A Lower Limit for the Ground State of the Helium Atom

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A method of obtaining a lower limit for the ground state of any system in terms of the energy difference between the ground state and the next highest state is given. Applied to the helium atom this gives a rough value of $-6.2R$ as compared to the experimental value of -5.818R.

1.

LET the Schrödinger equation describing a system in the n'th state, having energy W_n be

$$H\psi_n = W_n\psi_n \tag{1}$$

where H is the energy operator. Then it is well known that

$$I_1 = \int \xi H\xi^* d\tau \geqq W_0 \tag{2}$$

where ξ is any function satisfying the condition $\int\xi\xi^* = 1$. This is the basis of the Ritz method in which one guesses at a function with suitable parameters which are adjusted so as to make I_1 a minimum. This method has been applied by Kellner[1] and Hylleraas[2] to the ground state of the helium atom, who obtain values only a few hundredths of a percent above the experimental value. Such agreement does not necessarily mean that the true theoretical value agrees with the experimental value, although it is quite certain that this is so in this case. Nevertheless, in many cases it would be valuable to have a lower limit for the ground state. We assume ξ (ξ is taken to be real for simplicity) to be an approximate solution of the Schrödinger equation in the ground state. Analytically this means that $a_1, a_2, \cdots, a_n, \cdots$, are small compared to a_0 in the expansion

$$\xi = a_0\psi_0 + a_1\psi_1 + \cdots a_n\psi_n \cdots \tag{3}$$

where

$$\sum_{n=0}^{\infty} a_n^2 = 1. \tag{4}$$

Now

$$I_1 = \int \xi H\xi d\tau = \sum_{n=0}^{\infty} W_n a_n^2 \tag{5}$$

[1] Kellner, Zeits. f. Physik **44**, 91 (1927).
[2] Hylleraas, Zeits. f. Physik **48**, 469 (1928).

in virtue of the orthogonality properties of the ψ's

$$\int \psi_n \psi_m^* d\tau = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}. \tag{6}$$

We shall suppose the W's are arranged in order, so that

$$W_0 < W_1 < W_2 \cdots .$$

Using Eq. (4) we have

$$I_1 = W_0 + \sum_{n=1}^{\infty} (W_n - W_0) a_n^2. \tag{7}$$

Note that

$$\sum_{n=1}^{\infty} (W_n - W_0) a_n^2 = \Delta_1 \geqq 0. \tag{8}$$

Making use of our assumption about ξ so that we may neglect powers of a_n higher than the second, we have

$$I_1^2 = W_0^2 + 2W_0 \sum_{n=1}^{\infty} (W_n - W_0) a_n^2. \tag{9}$$

Let

$$\int \xi H^2 \xi d\tau = I_2 = \sum_{n=0}^{\infty} a_n^2 W_n^2 = W_0^2 + \sum_{n=1}^{\infty} (W_n^2 - W_0^2) a_n^2. \tag{10}$$

Now

$$I_2 - I_1^2 = \Delta_2 = \sum_{n=1}^{\infty} (W_n - W_0)^2 a_n^2 \geqq 0. \tag{11}$$

$$\Delta_1 \leqq \Delta_2 / W_1 - W_0. \tag{12}$$

Hence substituting in Eq. (7) we obtain our fundamental equation

$$I_1 - \frac{\Delta_2}{W_1 - W_0} \leqq W_0. \tag{13}$$

2. Application to Helium

We have

$$H = - a_0 e^2 / 2(\Delta_1 + \Delta_2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \tag{14}$$

where a_0 is the first Bohr orbit $a_0 = h^2/4\pi m e^2$, Ze the charge on the nucleus, and r_1 and r_2 the radial distances of the two electrons from the nucleus. We take for ξ the hydrogen eigenfunction of the ground state

$$\xi = \frac{\alpha^3}{\pi} e^{-\alpha(r_1 + r_2)}$$

$$\alpha = \frac{Z}{a_0} \cdot$$

Now it is well known (see Frenkel, Einfuhrung in die Wellenmechanik) that

$$I_1 = W_H + e^2 \int \xi^2 \frac{1}{r_{12}} d\tau = W_H + \tfrac{5}{8}\alpha e^2 = -5.5R \tag{15}$$

$$W_H = -4e^2/a_0.$$

Also

$$I_2 = \int \xi H \left(W_H + \frac{e^2}{r_{12}} \right) \xi = W_H^2 + e^2 \int \xi^2 \frac{1}{r_{12}} d\tau$$
$$- a_0 e^2/2 \int \xi (\Delta_1 + \Delta_2) \left(\frac{e^2}{r_{12}} \xi \right) d\tau$$
$$+ \int \xi^2 \frac{e^2}{r_{12}} \left(-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right) d\tau. \tag{16}$$

Now by Green's theorem, since the surface integrals vanish

$$\int \xi (\Delta_1 + \Delta_2) \left(\frac{e^2}{r_{12}} \xi \right) d\tau = \int \frac{e^2}{r_{12}} \xi (\Delta_1 + \Delta_2) \xi d\tau. \tag{17}$$

Hence

$$I_2 = W_H^2 + 2e^2 \int \xi^2 \frac{1}{r_{12}} d\tau + e^4 \int \xi^2 \frac{1}{r_{12}^2} d\tau \tag{18}$$

and

$$I_2 - I_1^2 = \Delta_2 = e^4 \int \xi^2 \frac{1}{r_{12}^2} - e^4 \left[\int \xi^2 \frac{1}{r_{12}} d\tau \right]^2. \tag{19}$$

Being unable to obtain its exact value, it was found that

$$e^4 \int \xi^2 \frac{1}{r_{12}^2} \approx 7/16 e^4 \alpha^2$$

$$\Delta_2 \approx 3/64 e^4 \alpha^2.$$

While there are methods of obtaining the theoretical value of $W_1 - W_0$ to a sufficiently good approximation, we take the experimental value $W_1 - W_0 = 16$ volts $= 0.56\, e^2/a_0$. We thus obtain

$$\frac{\Delta_2}{W_1 - W_0} \approx 0.34 e^2/a_0 = 0.68R$$

$$I_1 - 0.68R = -6.2R.$$

This may be compared with the experimental value of $-5.818R$.

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